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Total No. of Pages: 4

M.Sc. (Part-II) (Semester-III) (CBCS) Examination, April-2019 ORGANIC CHEMISTRY

Organic Reaction Mechanism (Paper - IX)

Sub. Code: 60840

Day and Date: Monday, 1 - 04 - 2019 Total Marks: 80

Time: 3.00 p.m. to 6.00 p.m.

Instructions:

- 1) Attempt in all five questions.
- 2) Section-I is compulsory.
- 3) All questions carry equal marks.
- 4) Answer to the all questions (Section-I,II,III) Should written in the same answer book.
- 5) Figure to the right indicate marks.
- 6) Attempt at least two questions from section-II and any two questions from Section-III.
- 7) Use of log table and calculator is allowed.

SECTION-I

Q1) Answer the following.

[16]

- a) What are Norrish type I reactions?
- b) Why does reaction of benzophenone with cis-stilbene results in the dimerization instead of oxetane formation?
- c) What do you mean by Di-Pi methane rearrangements?
- d) Mention the name of any one compound used for photoreduction of ketones.
- e) Draw the LUMO of 1,3,5-hexatriene for photochemically induced reaction conditions.
- f) Which sigmnatropic rearrangement is involved in Cope rearrangement?
- g) Write the structures of any two nitrogen ylides.
- h) Write a reaction confirming that Diels-Alder reactions are stereospecific?

P.T.O.

- i) Which technique is used to confirm exact bond cleavage during hydrolysis of esters?
- j) State True or False: Dimerization of cyclopentadiene is an example of 2nd order reaction.
- k) Give an example of reversible reaction.
- 1) What is an activated complex.
- m) Define exactly the term "reaction mechanism".
- n) Why does the rate of reaction usually increase with increase in temperature?
- o) What is Wolff rearrangement?
- p) Which reaction is commonly employed for the synthesis of lactones?

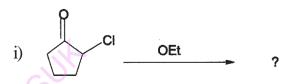
SECTION - II

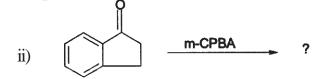
- Q2) a) Explain the following non-kinetic methods employed for determining reaction mechanism. [8]
 - i) Trapping of intermediates
 - ii) Cross-over experiments
 - iii) Evidence from reaction catalysis
 - b) Describe the study of following reactions by kinetic methods used for determining reaction mechanism: [8]
 - i) Reversible reactions
 - ii) Third order reactions
- Q3) a) What are phosphorus ylides? Explain their applications in organic synthesis. [8]
 - b) Explain the following:

[8]

- i) Favorskii reaction
- ii) Dienone-Phenol rearrangement

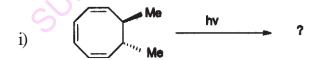
Q4) a) Write the products of following reactions giving suitable mechanism.[8]





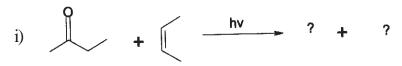
iii)
$$OH OH OH OH OH_{2}$$
 ?

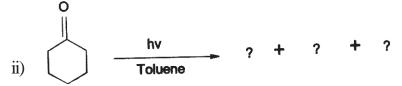
b) Write the products of the following reactions. Identify the pericyclic reaction involved in each case. [8]

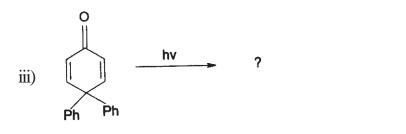


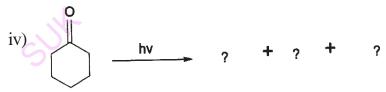
SECTION - III

- Q5) a) Explain the photo-addition of carbonyl compounds with olefins in the synthesis of oxetanes. [8]
 - b) Predict the products giving suitable mechanism. [8]









- **Q6**) a) Explain the correlation diagram for Diels-Alder reaction. [8]
 - b) Derive Woodward-Hofmann rules for electrocyclic reactions with a suitable example. [8]
- Q7) Write notes on any four. [16]
 - a) Photodimerization reactions.
 - b) Steady state approximation in conjugative reactions.
 - c) Baeyer-Villiger oxidation.
 - d) Sulphur ylides.
 - e) Norrish type II reactions.



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Total No. of Pages: 4

Total Marks: 80

M.Sc. (Part - II) (Semester - III) Examination, November - 2019 ORGANIC CHEMISTRY (CBCS) (Paper - IX)

Organic Reaction Mechanism

Sub. Code: 60840

Day and Date : Friday, 08 - 11 - 2019

Time: 11.00 a.m. to 02.00 p.m.

Instructions:

- 1) Attempt in all five questions.
- 2) Section I is compulsory.
- 3) All questions carry equal marks.
- 4) Answer to the all questions (Section I, II, III) should written in the same answer book.
- 5) Figure to the right indicate marks.
- 6) Attempt at least two questions from Section II and any two questions from Section III.
- 7) Use of log table and calculator is allowed.

SECTION-I

Q1) Answer the following:

- a) Enlist three types of pericyclic reactions.
- b) Mention any two photosensitizers.
- c) Why gamma-H is abstracted during Norrish type II reactions?
- d) Mention the name of any one compound used for photoreduction of ketones.
- e) Draw the HOMO of 1,3,5-hexatriene for thermally induced reaction conditions.
- f) Mention any one reaction involving [3,3] sigmatropic rearrangement.
- g) What is singlet oxygen?
- h) What type of bonding is present in phosphorus ylides?

SF - 341What are cycloaddition reactions? i) Write the rate equation for the first order reactions. j) What are parallel reactions? k) Define activated complex. 1) Give an example of isotope labelling technique. m) Write the structures of any two sulfur ylides. n) What is Smiles rearrangement? o) Mention the name of most commonly used per acid for Baeyer-Villiger p) oxidation. **SECTION-II Q2**) a) Explain the following non-kinetic methods used for determining reaction mechanism. [8] i) Cross-over experiments. ii) Testing of possible intermediates. Isotope labelling. iii) b) Describe the study of following reactions by kinetic methods used for determining reaction mechanism: [8] Reversible reactions. i) Second order reactions. ii) Explain the synthetic utility of phosphorus ylides in organic synthesis. **Q3**) a)

Dienone-Phenol rearrangement.

Baeyer-Villiger oxidation.

Explain the following:

b)

[8]

[8]

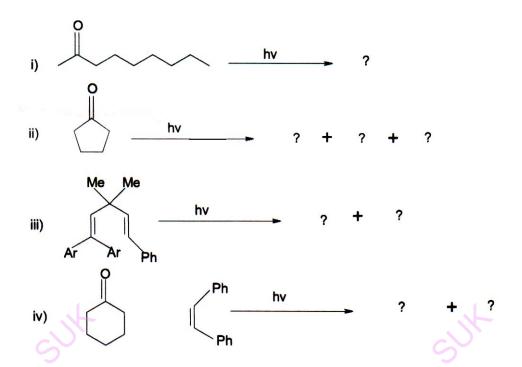
 $\it Q4$) a) Write the products of following reactions giving suitable mechanism. [8]

ii) $\begin{array}{c} & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\$

b) Write the products of the following reactions. Identify the pericyclic reaction involved in each case. [8]

SECTION-III

- **Q5**) a) Explain Paterno-Buchi reactions giving suitable examples. [8]
 - b) Predict the products giving suitable mechanism. [8]



- **Q6**) a) State the Woodward-Hofmann rules for electrocyclic reactions and discuss its application to [4n+2] Π electron systems. [10]
 - b) What are sigmatropic rearrangements? Give an account of Cope rearrangement. [6]
- Q7) Write notes on any four:

- a) Norrish type II reactions.
- b) Trapping of intermediates.
- c) Wolff rearrangement.
- d) Nitrogen ylides.
- e) Photoreduction of ketones.



Total No. of Pages: 4

Seat No.

M.Sc. (Part - II) (Semester - III) (CBCS) Examination, November - 2019

ORGANIC CHEMISTRY (Revised)

OCH 3.1 : Organic Reaction Mechanism (Paper - IX) Sub. Code : 74995

Day and Date : Friday, 08 - 11 - 2019 Total Marks : 80

Time: 11.00 a.m. to 02.00 p.m.

Instructions: 1) **Question No. 1 is compulsory.**

- 2) Select any two questions from each section.
- 3) Answer to the all questions must be written in the same answer book.
- 4) All questions carry equal marks.
- 5) Figures to the right indicate full marks.

Q1) a) Answer the following:

- i) What is Sandmeyer reaction?
- ii) Which method is used to know whether reaction is intermolecular or intramolecular rearrangement?
- iii) Mention any two photosensitizers.
- iv) Which method can be used to know the exact bond cleavage during hydrolysis of esters?
- v) Which metal is most commonly used for alkyne metahesis reactions?
- vi) Mention two factors that decided the stereochemical outcome of electrocyclic reactions?
- vii) What is kinetic isotope effect?
- viii) State True or False: Corey-Chaykovsky reaction involves sulfur ylides.

- ix) Draw the HOMO of 1, 3, 5-hexatriene under thermal conditions?
- x) Which sigmatropic rearrangement is involved in Ene reaction?
- b) Write the products of the following reactions.

SECTION - I

- Q2) Elaborate various kinetic methods of determining reaction mechanism. [16]
- Q3) a) Explain the correlation diagram for electrocyclic reaction with suitable example.[8]
 - b) Describe [4+2] cycloaddition reaction by using FMO approach. [8]

Q4) a) Write the products of following pericyclic reactions giving necessary selection rule.



b) Give an account on Hammett equation? Explain the significance of sigma and rho values. [8]

SECTION - II

- Q5) a) What are phosphorus ylides? Explain the synthetic utility of phosphorus ylides.[8]
 - b) Explain the following reactions. [8]
 - i) Weinreb ketone synthesis
 - ii) Corey-Kim oxidation
- **Q6**) a) Explain the mechanism of the Acyloin condensation and autooxidation reaction. [8]
 - b) Write the products giving mechanism: [8]

Q7) Write notes on (any four):

[16]

- a) Cross-over experiments
- b) Nitrogen ylides
- c) Sigmatropic rearrangements
- d) Coupling of alkynes
- e) Alkyne metathesis reaction

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Total No. of Pages: 3

M.Sc. (Part - II) **Examination, April - 2019**

ORGANIC CHEMISTRY Reaction Mechanism and Theoretical Organic Chemistry (Paper-V) Sub. Code: 49593 Day and Date : Monday, 1 - 04 - 2019 Total Marks: 100 Time: 3.00 p.m. to 6.00 p.m. **Instructions:** 1) Attempt in all five questions. Answer to the all questions must be written in the same answer book. 2) 3) Figure to the right indicate marks. Q1) Answer the following (any four): [20] Explain non classical carbocation. a) b) Explain the catalytic cycle of Suzuki reaction. Explain the photochemistry of vision. c) Explain concept of alternant and non - alternant hydrocarbons. d) Mention the applications of crown ethers. e) Write a note on detection of free radicals by ESR spectroscopy. f) What are ylides? Give the preparative methods and synthetic utility of **Q2)** a) phosphorus ylides? [10]Discuss the following reactions. [10]b) Favorskii reaction i) Baeyer - Villiger oxidation ii) OR Explain the formation, stability and reactivity of carbenes. a) [10]Discuss the following reactions. [10]b) Chichibabin reaction i) Michael reaction

Q3) a) Describe Norrish type II reactions in details.

[10]

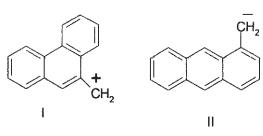
b) Give the products of the following photochemical reactions with mechanism. [10]

OR

- a) Explain Paterno Buchi reaction. [10]
- b) Write notes on: [10]
 - i) Cis-trans isomerization
 - ii) Photo-Fries rearrangement
- Q4) a) Using pertubational molecular orbital (PMO) theory, calculate the reactivity index (NE) when naphthalene undergoes SE reactions at position 1 and 2. [10]
 - b) i) Calculate the delocalization energy in the following. [5]



ii) Determine the charge density in the following. [5]



OR

a) Explain the following reactions giving suitable mechanism: [10]

- i) Acyloin condensation.
- ii) Sandmeyers reaction.
- b) Predict the products giving suitable mechanism.

[10]

i)
$$\bigcirc$$
 COOAg + Br₂ \longrightarrow ?

Q5) a) Give an account on the structure and properties of ferrocene. [10]

- b) Write a note on. [10]
 - i) Fullerenes
 - ii) Annulenes

OR

- a) Give an account on the various methods of preparation of tropylium salts. [10]
- b) Write a note on. [10]
 - i) Auto oxidation
 - ii) Hunsdiecker reaction







Total No. of Pages :3



M.Sc. (Part - II) (Semester - III) Examination, November - 2018 ORGANIC CHEMISTRY (Paper - IX) Organic Reaction Mechanism (CBCS)

Sub. Code: 60840

Day and Date: Thursday, 22 - 11 - 2018

Total Marks: 80

Time: 10.30 a.m. to 01.30 p.m.

Instructions:

- 1) Attempt in all five questions.
- 2) Question No. 1 is compulsory.
- 3) All questions carry equal marks.
- 4) Answer to the all questions (Section I and II) must be written in the same answer book.
- 5) Figures to the right indicate full marks.
- 6) Attempt at least two questions from Section-I and any two questions from Section II.
- **Q1)** A) Answer the following (One mark each).

- i) Mention any two photosensitizers.
- ii) What is cope rearrangement?
- iii) What is Inter System Conversation?
- iv) Define singlet oxygen.
- v) Which reaction can be used to prepare lactones?
- vi) What is isotope labelling?
- vii) What are sigma (σ) values?
- viii) Enlist the types of pericyclic reactions.
- ix) Which factors decide the stereochemistry of electrocyclic reactions?
- x) Define activated complex.

B) Write the products:

xii)
$$Ph_3P=CH_2$$
 ?

xiii) hv ?

xiv) $heat$?

xv) hv ?

xvi) hv ?

SECTION-I

- Q2) Give an account on various non kinetic methods of determining reaction mechanism.[16]
- **Q3)** a) Give the preparative methods and synthetic utility of sulfur ylides? [8]
 - b) Explain the following reactions. [8]
 - i) Dienone-Phenol rearrangement.
 - ii) Favorskii reactions.
- **Q4)** a) State and explain Woodward Hoffmann rules of the conservation of orbital symmetry for electrocylic reactions. [10]
 - b) Explain [3,3] sigmatropic rearrangements. [6]

SECTION-II

Q5) a) Describe Paterno-Buchi reactions.

[8] [8]

[8]

- b) Write the products of following reactions with mechanism.

 - ii) hv ?
 - iii) OH ?
 - iv) m-CPBA ?
- **Q6)** a) Give a brief account no Norrish type II reactions.
 - b) Give the products of the following photochemical reactions with mechanism. [8]
 - i) + [CI hv ?
 - ii) hv ?
 - iii) Me Me hv ?
 - $\frac{hv}{O_2} ?$
- **Q7)** Short notes: (any four)

- a) Cycloaddition reactions.
- b) Phosphorus ylides.
- c) Hammett equation.
- d) Kinetic isotope effect.
- e) Photochemical cis-trans isomerization.

